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## New High Energy Density Small Ring Systems

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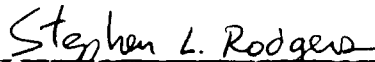
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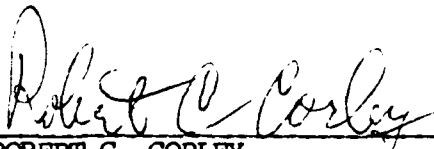


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A theoretical research investigation of four-atom light element species has been undertaken in order to find propellants with revolutionary performance. The ab initio calculations show that the rhombic geometry is a global minima on the potential energy surface of  $B_2Li_2$  dicarbides and diborides composed of H, Li, Be, B, C, and Si. By means of bond-stretch isomerism, bonding pattern change, these rhombic species can store significant amounts of energy - 87 kcal/mole to 122 kcal/mole. Only in the case of  $B_2Be_2$  was the tetrahedral form stable. All of the four-atom species found stable by this investigation are estimated to provide high specific impulses.

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## SUMMARY

Theoretical ab initio calculations have been carried out on tetraatomic systems in the search for advanced chemical propellants. In the approach to identify systems with revolutionary specific impulses ( $I_{sp} > 500$  sec) we concentrated on molecular systems that are (a) composed of elements with high combustion energies, (b) that have a high degree of unsaturation (H-deficient), and (c) are very strained (inverted geometries of carbon and boron). The research efforts were focussed on cyclic tetraatomics to develop an understanding of their structural, energetic, and electronic properties.

The rhombic forms of  $C_4$ ,  $C_4H^+$ , and  $C_4H_2^{2+}$  were used as parent molecules. Although the linear triplet  $C_4$  form has been observed, there are experimental indications for the existence of a rhombic isomer (the two structures are of equal stability). However, for the diprotonated species the coexistence of the linear and rhombic forms in the gas phase is unequivocal and based on charge separations that give excellent agreement with theoretical data. The estimated heat of formation of 726 kcal/mol for rhombic  $C_4H_2^{2+}$  is one of the highest for a dication.

The question has been addressed whether other elemental combinations could render similar systems of high energy. Related to this question we have developed an understanding of the bonding pattern of these molecules and how their energy content may be manipulated.

A survey of light four-atom systems at the HF/6-31G\* level of theory has been conducted on dicarbides and diborides with ligands ranging from Li, Be, BeH, BH, C, CH, AlH, to Si. Of the dicarbides 24 different rhombic structures are minima on the potential energy surface and 21 diborides have been characterized as are minima. While the distance between the bridgehead carbons (borons) is virtually constant throughout all dicarbides (diborides) their bonding varies significantly. To evaluate the viability of rhombic forms also tetrahedral diboride combinations have been explored. Of the 24 diborides only three light elemental combinations are minima. These are  $B_2Li_2$ ,  $B_2Be_2$ , and  $B_2Be_2H^-$ .

To inspect in more detail the theoretical levels required to describe rhombic tetraatomics and to evaluate their energetic properties, full potential energy surface scans have been performed on  $C_2Si_2$ ,  $B_2Be_2$ , and  $B_2Li_2$ . The latter two light element systems have estimated  $I_{sp}$  values of 646 and 531 sec, respectively. These values are based on MP4/6-31G\* binding energies. The calculations show that electron correlation has a large influence on

the relative stabilities and binding energies, but only marginally influences the geometrical parameters of isomeric structures. To inspect the chemical properties of such systems toward hydrogen, we have investigated the potential energy surface of  $B_2Be_2H_2$ .

Bonding patterns have been evaluated by analysis of the electron densities. It has been found that no transannular bond exists between the 1.523 Å separated bridgehead carbons of  $C_4$ . However a small reduction in length results in CC bond formation, or conversely lengthening the CC distance results in further depletion of electron density in the center of the rhombic structure as is the case in  $C_4H^+$  and  $C_4H_2^{2+}$ .

Because of the variation in bridgehead CC (and BB) overlap, and the notable lack of a CC bond in  $C_4$ , we have investigated whether breaking of the transannular CC (and BB) bond can render vibrational stable species of higher energy. Such a mechanism, bond stretch isomerism, has been found in several systems. In the case of  $C_2Si_2$ , which is isovalent with  $C_4$ , such a rhombic structure is found 78 kcal/mol higher in energy than the global rhombic minimum. Similarly, in the case of  $B_2Be_2$  a rhombic form is found 60.6 kcal/mol higher in energy than the global minimum. The barrier for interconversion between the two rhombic structure has not been determined but is estimated to be high because it would represent a symmetry forbidden process. This may suggest that the high energy rhombic forms have substantial kinetic stability.

Structures containing lithium atoms like  $B_2Li_2$  have ionic bonds. Therefore the properties of  $B_2Li_2$  and  $B_2Be_2$  differ greatly. In collaboration with Michels we investigated how ionic complexes may render high energy materials. It was found that in the  $Li_3H$  the  $H^-$  anion is complexed to the side of triangular  $Li_3^+$  cation unit (i.e. rendering rhombic  $Li_3H$ ), thereby leaving the properties of this  $Li_3^+$  cation unit in tact.

An investigation exploring the potential of bridging diboride units with Al atoms has been initiated. Because of the general lack of theoretical information available on Al-Al interactions, as compared with that on B-B bonds, exploratory studies have been conducted on  $Al_2H_6$  as well as on the recently observed  $Ga_2H_6$  and  $Ga_2H_4$ . These studies focussed on determining binding energies and the influences governing ionic versus covalent bonding.

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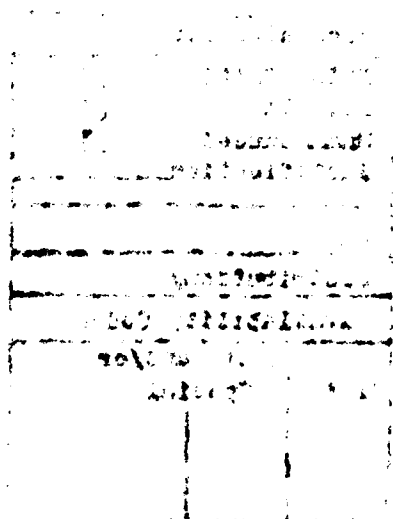
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## INTRODUCTION

For decades chemists have been intrigued by small ring compounds. Many studies have been devoted to highly strained, small hydrocarbons,<sup>1</sup> carboranes,<sup>2</sup> and silicon derivatives.<sup>3</sup> Although giant steps have been made in materials science and there is an increasing understanding of Li clusters, B clusters, Be clusters, C clusters and Si clusters, the information concerning bonding and energetic properties of mixed cluster compounds remains very limited. In the past three years, we systematically investigated a series of over 50 tetraatomic diborides and dicarbides by ab initio molecular orbital theory. In this report, we describe the results of this theoretical survey study on potentially high energy four-membered ring compounds composed of the elements Li, Be, B, C, Al, and Si.

The foundation for developing high energy density systems is often based on:

- (a) increasing the unsaturation by stripping molecules of all their hydrogens.
- (b) increasing the strain energy by inverting the carbon (and boron) geometries.

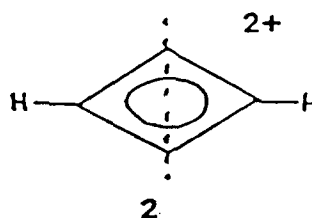
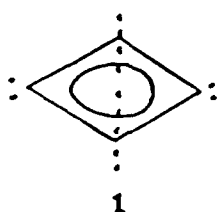
For example, there are numerous strained hydrocarbons that have either inverted tetra-coordinated ( $sp^3$ ) geometries<sup>4</sup> or pyramidelized olefinic bonds. In this investigation, we capitalized on the properties of inverted tricoordinated ( $sp^2$ ) boron and carbon atoms.<sup>5</sup> Below follows a description which uses  $C_4$  as an example of how we developed such unsaturated systems with inverted carbon geometries, to find highly energetic, yet stable, strained ring systems.

### Energetic Four-Membered Ring Structures; $C_4$ .

The expected increase in energy on depletion of hydrogen from the cyclic  $C_4$ -frame is evident from the HF/6-31G\* data listed in Table 1. At this level of theory, the heat of formation  $\Delta H_f^\circ$  of rhombic  $C_4$  ( $D_{2h}$ ) is 228 kcal/mol (estimated from calculated heats of hydrogenation in combination with experimental reference points—). The deduction of this value includes corrections for  $\Delta$  zero point energy, hydrogenation (each 6.4 kcal/mol),  $\Delta H_f^\circ(0-298^\circ)$ , and for differences (7 kcal/mol) between calculated and experimental values.<sup>11</sup> The  $\Delta H_f^\circ$  value of 228 kcal/mol for rhombic  $C_4$  (inverted  $sp^2$ ) is large compared to the heat of formation of 89 kcal/mol (HF/6-31G\*) for stable [1.1.1]propellane (inverted  $sp^3$ ), which has a strain energy SE of 103 kcal/mol.<sup>10</sup> The experimentally known  $C_4H_2^{2+}$  dication, with the highest  $\Delta H_f^\circ$  of any cationic system (726 kcal/mol), provides further evidence of this contrast.<sup>12</sup> In this investigation we made use of this contrast

TABLE 1. 6-31G\* energies (in a.u.), heats of formation ( $\Delta H_f$ , in kcal/mol), and strain energies (SE, in kcal/mol) for  $C_4$  structures.

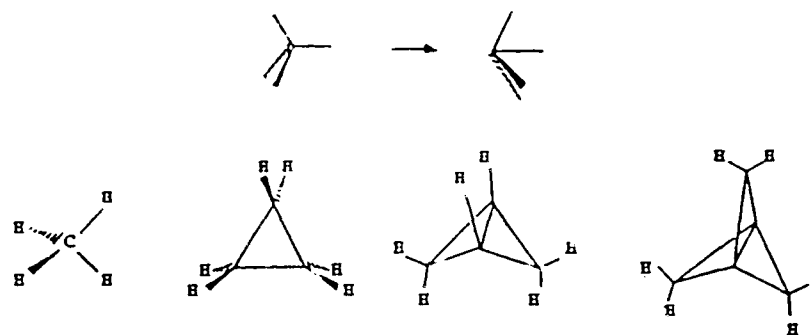
Compound	Formula	Energy	$\Delta H_f$	SE
1 <sup>4,6</sup>	$C_4$	-151.14598	228	
2 <sup>6</sup>	$C_4H_2^{2+}$	-151.53998	726	
Cyclobutadiene dication <sup>7</sup>	$C_4H_4^{2+}$	-152.91650	623	
Bicyclo[1.1.0]butene <sup>8</sup>	$C_4H_4$	-153.58016	142	127
1,3-Cyclobutadiene <sup>9</sup>	$C_4H_4$	-153.64120	103	65
Bicyclo[1.1.0]butane <sup>8</sup>	$C_4H_6$	-154.87176	51.9	65
Cyclobutene <sup>10</sup>	$C_4H_6$	-154.89962	37.5	29
Cyclobutane <sup>10</sup>	$C_4H_8$	-156.09703	6.8	26
Hydrogen <sup>8</sup>	$H_2$	-1.12683		



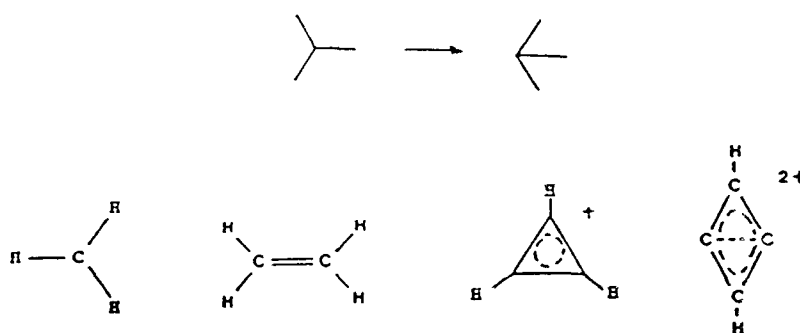
between  $C_4$  and [1.1.1]propellane to design over forty, stable, high energy, tetraatomic species.

### Rhombic Tetracarbon, $C_4$ .

We<sup>6</sup> and others<sup>13</sup> have demonstrated that rhombic  $C_4$  (1) is of nearly the same energy as triplet linear  $C_4$ . The unusual stability of cyclic  $C_4$  can be explained by inspection of its molecular orbital framework.<sup>6</sup> The highest occupied molecular orbital, HOMO, is a non-bonding  $\sigma$ -orbital between the bridgehead carbons with the electron density located outside the molecule. Hence, the HOMO does not contribute to ring strain. The stabilization of rhombic  $C_4$  results from aromatic  $\pi$  bonding; a  $\sigma$ -bridged- $\pi$  MO is also present. Besides its  $\sigma$  skeleton, the molecule has two lone electron pairs. In simple Lewis terms, the bonding of both bridgehead C atoms in  $C_4$  can be described as follows: (a) two valence electrons are involved in ring C-C bonding, (b) the third electron participates in aromatic ring  $\pi$  bonding, while (c) the fourth electron is involved in  $\sigma$  nonbonding.



Scheme I. Inverted tetracoordinate geometries at carbon



Scheme II. Inverted tricoordinate geometries at carbon

### Diprotonated Rhombic $C_4$ .

Our study on the  $C_4H_2^{2+}$  dication underscores the validity of inverted planar tricoordinate carbons.<sup>6</sup> Cyclic  $C_4H_2^{2+}$  (2,  $D_{2d}$ ) is only 13.3 kcal/mol (MP3/6-31G\*) less stable than its triplet linear diacetylenic isomer, despite the anticipated strong electrostatic charge-charge repulsion.<sup>12a</sup> Both isomers have been observed in the gas phase.<sup>12a</sup> An alternative (but empirical) explanation for the stability of rhombic  $C_4H_2^{2+}$  can be given along the lines shown for strain build-up in saturated hydrocarbons, now adapted for olefins (Scheme I and II). Stepwise replacement of the vicinal hydrogens from the parent ethylene by  $CH^+$ -groups gives either the cyclopropenyl cation or cyclic  $C_4H_2^{2+}$ , (note that in this series the tricoordinate carbon is completely inverted, while the  $2\pi$  stabilization is maintained!).

## TECHNICAL DISCUSSION

The question this investigation addressed is whether the inverted tricoordinate geometry concept developed for high energy density small ring hydrocarbons can be expanded to include other elements. There are two important aspects to consider.

- (a) Do the characteristics of an inverted planar tricoordinate carbon change using bridging elements other than carbon?
- (b) Can the bridgehead carbons be replaced by other elements while maintaining the high energy density properties of the system?

To address these questions we discuss a large number of tetraatomic rhombic and tetrahedral structures and will analyze several small clusters. These latter potential energy surface studies are presented in a summarized fashion. A complete analysis for each cluster is presented in the appendices, which have appeared or are to appear in the scientific literature.

### RHOMBIC STRUCTURES — Structures and Energies

**Tetraatomic Dicarbides.** We have examined at the 6-31G\* level of theory 25 rhombic dicarbides with ligands ranging from Li, Be, BH, C, AlH, and Si, in virtually all combinations. The data are listed in Table 2. This group of planar structures includes anions, cations, and dipolar molecules. Of these 25 dicarbides, 24 are *minima* on the 6-31G\* potential energy surface, as indicated by the zero number of imaginary frequencies. These data strongly support the viability of rhombic structures that contain inverted tricoordinate carbons irrespective of the type of bridging ligand.

Similarly impressive in these dicarbides is their rather short C-C distance which has an average value of only 1.457 Å (dianions excluded). This is unexpected because of the range of bridging elements involved. Inspection of the Mulliken overlap population indeed shows that the nature of bonding between the carbons must vary significantly. Representative values are -0.236 for  $C_4H_2^{2+}$ , -0.063 for  $C_4$ , and +0.306 for  $C_2Be_2$ . However, the Mulliken population analyses is subject to criticism, in particular for unsymmetrical bonding arrangements, and hence can not rigorously answer what types of bonding are operative in the dicarbides. We attempted Weinhold's superior Natural Bond Order approach,<sup>14,15</sup> but found too many complications in using this method due to ionicity in the rhombics. The Bader electron analysis, which we will describe in the following section on bonding patterns, allowed us to characterize the bonding in these molecules.

**TABLE 2.** Rhombic Dicarbides RHF/6-31G\* Energies, NIMAG, and Geometrical Data.

Structure X-C <sub>2</sub> -Y	Energy	Nimag	Bond Distances		
			C—C	C—X	C—Y
Li-(C <sub>2</sub> )-Li	-90.37222	0	1.249	2.108	2.108
Li-(C <sub>2</sub> )-Be	-97.58752	0	1.436	1.907	1.571
Li-(C <sub>2</sub> )-BH	-108.30443	0	1.426	1.881	1.472
Li-(C <sub>2</sub> )-CH	-121.50728	0	1.470	1.968	1.348
Li-(C <sub>2</sub> )-C:	-120.84757	0	1.402	1.880	1.418
Li-(C <sub>2</sub> )-AlH	-325.48897	1	1.374	1.922	1.899
Be-(C <sub>2</sub> )-Be	-104.79129	0	1.459	1.565	1.565
Be-(C <sub>2</sub> )-BH	-115.47831	0	1.445	1.558	1.473
Be-(C <sub>2</sub> )-CH	-128.39388	0	1.484	1.619	1.345
Be-(C <sub>2</sub> )-C:	-127.98366	0	1.418	1.563	1.421
Be-(C <sub>2</sub> )-AlH	-332.67417	0	1.451	1.561	1.857
BeH-(C <sub>2</sub> )-BH	-116.13470	0	1.449	1.670	1.470
BeH-(C <sub>2</sub> )-CH	-129.26994	0	1.501	1.739	1.339
BeH-(C <sub>2</sub> )-C:	-128.66892	0	1.433	1.677	1.408
BeH-(C <sub>2</sub> )-AlH	-333.31024	0	1.419	1.683	1.853
BH-(C <sub>2</sub> )-BH	-126.15541	0	1.470	1.470	1.470
BH-(C <sub>2</sub> )-CH	-139.01220	0	1.529	1.526	1.345
BH-(C <sub>2</sub> )-C:	-138.65329	0	1.462	1.479	1.418
BH-(C <sub>2</sub> )-AlH	-343.35876	0	1.449	1.470	1.848
CH-(C <sub>2</sub> )-CH	-151.53998	0	1.593	1.386	1.386
CH-(C <sub>2</sub> )-C:	-151.45693	0	1.520	1.352	1.472
CH-(C <sub>2</sub> )-AlH	-356.27607	0	1.494	1.342	1.919
C:-(C <sub>2</sub> )-C:	-151.14598	0	1.457	1.425	1.425
C:-(C <sub>2</sub> )-AlH	-355.86570	0	1.436	1.418	1.857
AlH-(C <sub>2</sub> )-AlH	-560.55536	0	1.436	1.858	1.858
:Si-(C <sub>2</sub> )-Si:	-653.41467	0	1.415	1.818	1.818
BH-(Si <sub>2</sub> )-BH	-628.24903	0	2.461	1.950	1.950
:C-(Si <sub>2</sub> )-C:	-649.77894	-	2.292	1.863	1.863
AlH-(Si <sub>2</sub> )-AlH	-1057.08620	-	2.628	2.337	2.337

**Tetraatomic Diborides.** We have examined at the HF/6-31G\* level of theory 28 rhombic diborides with ligands ranging from Li, Be, BH, C, AlH, and Si, in virtually all combinations. The 6-31G\* data for these systems, that contain two valence electrons less than the discussed dicarbides, are listed in Table 3. Like the planar dicarbides this group also includes anions, cations, and dipolar molecules. Of the 28 diborides, 21 are minima on the HF/6-31G\* potential energy surface, as indicated by the zero number of imaginary frequencies; the other 7 are transition structures. Similar to the dicarbides these data support the viability of rhombic structures now containing inverted tricoordinate borons with a large variety of bridging ligands.

Considering the two-electron difference with dicarbides these diborides have a relatively short average B-B distance of 1.833 Å. However, as will be shown, the bonding nature of these systems is entirely different from that in the dicarbides.

## BONDING PATTERNS

An understanding of the bonding nature in the rhombic structures can be obtained by analyzing the electron density ( $\rho$ ) properties of these molecules. Prof. R.F.W. Bader of McMaster University was so kind to provide us with the software that his research group has developed. A detailed description of his method and its applications can be found in the literature (also Appendix C).<sup>16</sup> However, a synopsis of the method assists in comprehending the figures in this report.

In short, the method is concerned with the electron density  $\rho$  although connections with molecular orbitals can be made. The programs EXTREME and PROAIM were interfaced with GAUSSIAN 86 and 88 and use the same basis sets. The properties of a molecular charge distribution, based on Bader's topological analysis of density of atoms in molecules, are summarized in terms of its critical points. These are points where the charge density is a maximum, a minimum, or a saddle of the gradient path of the gradient vector field i.e.,  $\nabla\rho = 0$ . A critical point is characterized by the signs of its three principal curvatures of  $\rho$  i.e.,  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ . A bond critical point (3,-1) has a minimum (positive curvature) in  $\rho$  on the bond path connecting two nuclei and two negative curvatures in orthogonal planes; the charge density has the appearance of a saddle. Ring critical points (3,+1) have one negative and two positive curvatures. Three positive curvatures (3,+3) define a minimum (cage critical point). The (3,-3) critical point represents atoms or nuclear attractors ("pseudo atoms") where all curvatures are positive. In the figures presented the connectivity of atoms via bond critical points are given (the molecular graphs) in both plots of the gradient vector field, (which give the separation of atoms in molecules by

TABLE 3. Rhombic Diborides RHF/6-31G\* Energies, NIMAG and Geometrical Data.

Structure X-B <sub>2</sub> -Y	Energy	Nimag	Bond Distances		
			B—B	B—X	B—Y
Li-(B <sub>2</sub> )-Li	-64.04676	0	1.540	2.197	2.197
Be-(B <sub>2</sub> )-Be	-78.33038	0	2.013	1.760	1.760
Be-(B <sub>2</sub> )-BeH	-78.95048	1	1.888	1.755	1.862
Be-(B <sub>2</sub> )-BH	-89.03080	0	1.809	1.753	1.598
Be-(B <sub>2</sub> )-CH	-102.02063	0	1.823	1.813	1.443
Be-(B <sub>2</sub> )-C:	-101.63581	0	1.863	1.754	1.383
Be-(B <sub>2</sub> )-AlH	-306.22846	1	1.997	1.756	2.040
Be-(B <sub>2</sub> )-Si:	-352.67586	0	1.790	1.758	1.911
BeH-(B <sub>2</sub> )-BH	-89.67334	1	1.742	1.870	1.594
BeH-(B <sub>2</sub> )-CH	-102.86362	0	1.787	1.937	1.445
BeH-(B <sub>2</sub> )-C:	-102.28936	0	1.765	1.906	1.39
BeH-(B <sub>2</sub> )-AlH	-306.86504	1	1.877	1.858	2.036
BeH-(B <sub>2</sub> )-Si:	-353.32652	1	1.734	1.881	1.920
BH-(B <sub>2</sub> )-BH	-99.72164	0	1.690	1.604	1.604
BH-(B <sub>2</sub> )-CH	-112.66014	0	1.719	1.658	1.444
BH-(B <sub>2</sub> )-C:	-112.28438	0	1.645	1.642	1.399
BH-(B <sub>2</sub> )-AlH	-316.93016	0	1.819	1.594	2.032
BH-(B <sub>2</sub> )-Si:	-363.35948	0	1.683	1.607	1.941
CH-(B <sub>2</sub> )-CH	-125.29859	0	1.740	1.482	1.482
CH-(B <sub>2</sub> )-C:	-125.15331	0	1.623	1.464	1.460
CH-(B <sub>2</sub> )-AlH	-329.91335	0	1.848	1.440	2.102
CH-(B <sub>2</sub> )-Si:	-376.30524	0	1.726	1.442	2.047
:C-(B <sub>2</sub> )-C:	-124.63404	1	1.752	1.420	1.420
:C-(B <sub>2</sub> )-Si:	-375.93214	0	1.689	1.392	2.004
:C-(B <sub>2</sub> )-AlH	-329.53246	0	1.813	1.382	2.037
AlH-(B <sub>2</sub> )-AlH	-534.12534	1	1.996	2.037	3.553
AlH-(B <sub>2</sub> )-Si:	-580.57306	0	1.778	2.037	1.910
:Si-(B <sub>2</sub> )-Si:	-627.00013	0	1.666	1.947	1.910

"zero flux" lines) and the Laplacian field of the charge density  $\nabla^2\rho$  (the sign of which also characterizes the polarity of a bond).

**Tetraatomic Dicarbides.** The variation of bonding possible in planar rhombic dicarbides can be illustrated in the neutral series  $C_2Li_2$ ,  $C_2Be_2$ ,  $C_2B_2$ , and  $C_4$ , which shows a gradual changeover from the fully ionic  $C_2Li_2$  system to the covalently bonded  $C_4$ . Figure 1 gives a representation of the gradient vector field of their charge density (HF/6-31G\*) in terms of the paths traced out by the vectors  $\nabla\rho$  and also displays the corresponding contour maps of the Laplacian of their charge density overlaid with bond paths.

The lithiums in  $C_2Li_2$  are bonded to the center of the C-C bond. In fact, the C-C bond path has three bond critical points and two "pseudo atoms" (nuclear attractors, (3,-3)). This unusual behavior can be interpreted as a C-C triple bond with a long path of virtually constant electron density. Recently, pseudo atoms were also found in studies by Bader and Gatti on Li and Na clusters.<sup>17</sup> They argued tentatively that these nuclear attractors may be associated with metallic behavior. However, our observations of these (3,-3) critical points in dicarbides and diborides (*vide infra*) may indicate a more universal behavior. In replacing Li for Be to give  $C_2Be_2$ , bond paths are found at the circumference of the rhombic structure, although there remains a high degree of ionicity. The results on  $C_2Be_2$  agree with those reported by Cremer and Schleyer.<sup>18</sup> The difference between  $C_2B_2$  and  $C_4$  reveals an interesting feature. While the zero-flux line of the bridging ligand in  $C_2B_2$  is clearly defining the boron, in  $C_4$  it is penetrating the rhombic structure. In fact, the two ring critical points (3,+1) and the bond critical point (3,-1) of the bridgehead-bridgehead C-C bond path in  $C_4$  nearly coalesce, an observation also made by Ritchie.<sup>19</sup> Evidently, the center of  $C_4$  represents a near catastrophe point. This means that a small perturbation of  $C_4$  can eliminate bonding between the bridgehead carbons, despite their short 1.457 Å (HF/6-31G\*) separation.

The change in bonding between the bridgehead carbons becomes even more pronounced in comparing the series  $C_4$ ,  $C_4H^+$ , and  $C_4H_2^{2+}$ . Their 6-31G\* transannular C-C distance are 1.523 (MP2), 1.520 (HF), and 1.593 Å (HF), respectively. The Laplacian of  $\rho$  for these systems are shown in Figure 2. From this Figure it is quite clear that there is electron depletion in the center of  $C_4H_2^{2+}$  and consequently this structure does not possess a transannular C-C bond.



Molecular Graphs of Dicarbides at the Molecular Plane

Laplacian plots of Dicarbides

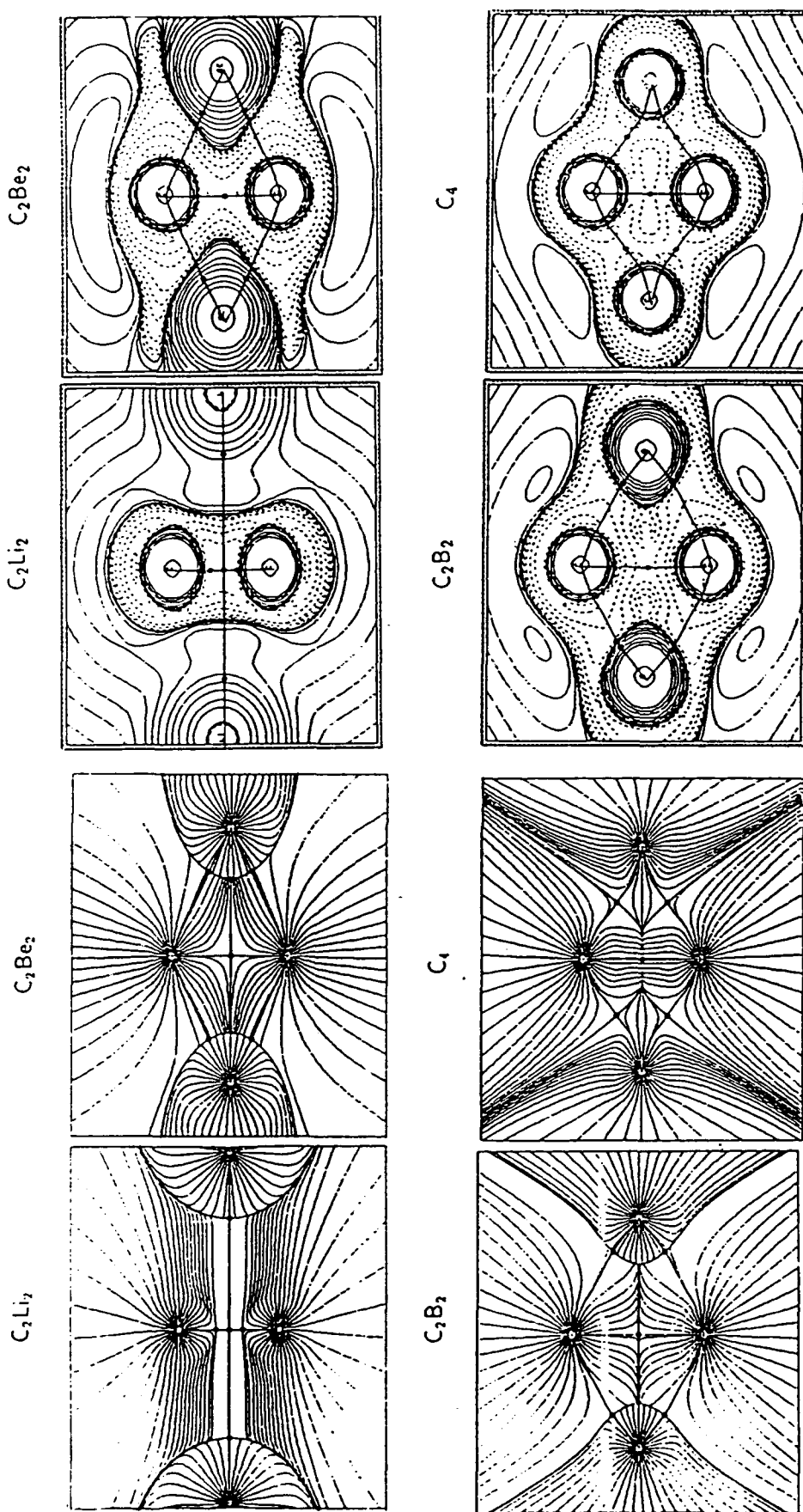


Figure 1. Gradient vector field and the Laplacian concentration of the HF/6-31G\* charge density of  $C_2Li_2$ ,  $C_2Be_2$ ,  $C_2B_2$ , and  $C_4$ .

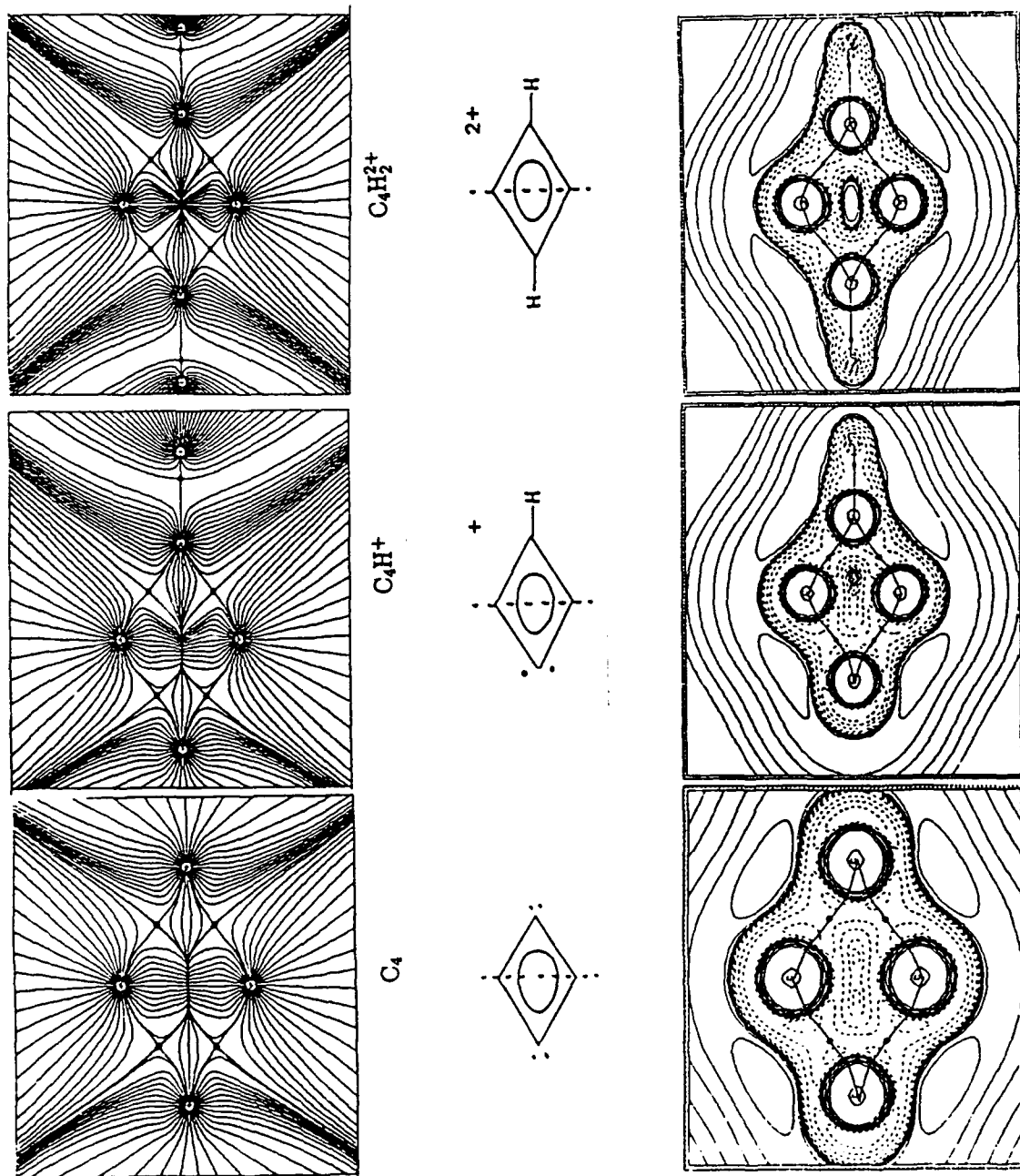


Figure 2. Gradient vector field and the Laplacian concentration of the HF/6-31G\* charge density of  $C_4$  (MP2),  $C_4H^+$ ,  $C_4H_2^{2+}$

**C<sub>4</sub> in more detail.** Because of the crucial position of C<sub>4</sub> in the discussed series of rhombic dicarbides, we wanted to study its properties in more detail. As mentioned, it seems that at the HF/6-31G\* level of theory the transannular C-C interaction changes from multiple C-C bonding in C<sub>2</sub>Li<sub>2</sub> to no C-C bonding in C<sub>4</sub>H<sub>2</sub><sup>2+</sup>. Because C<sub>4</sub> is the structure where this C-C bonding is lost (or formed), it seemed to us that an analysis of C<sub>4</sub> at higher levels of theory was desired. A brief summary of this study follows. The full analysis is given in a draft manuscript<sup>20</sup> in Appendix A.

The molecular orbital and topological electron density analysis of the MP2(Full)/6-31G\* optimized rhombic C<sub>4</sub> structure shows that there is no transannular C-C bond despite the 1.523 Å separation between the inverted tricoordinate carbons. The peripheral bonds are short (1.451 Å, bond order = 1.15) due to strong surface ( $\sigma$ ) and  $\pi$ -delocalization. This contrasts with [1.1.1]propellane, which at the same level of theory, does have bonding between the inverted tetracoordinate carbons which are separated by 1.592 Å.

**Diborides.** To demonstrate the difference in bonding behavior of diborides and dicarbides, we have analyzed the electron density properties of the planar rhombic forms of B<sub>2</sub>Li<sub>2</sub>, B<sub>2</sub>Be<sub>2</sub>, and B<sub>4</sub>. Figure 3 displays the gradient vector field of their charge density in terms of the paths traced out by the vectors  $\nabla\rho$  (left), while the contour maps of the Laplacian of their charge density overlaid with bond paths are given on the right hand side.

Some remarkable features are apparent. In the diborides the borons are bonded with two bond critical points (3,-1) located either on the same B-B bond path (separated by a pseudo atom) or on two separate B-B bond paths.

In the case of the covalent B<sub>4</sub> structure, the four ring B-B bond paths have two bond critical points each. The center of the molecule shows a depletion of charge with no bonding between the atoms (instead it is a (3,+1) ring critical point). The bonding pattern in planar B<sub>2</sub>Be<sub>2</sub> is different. The two borons are bonded by two curved bond paths with an "electron density hole" (i.e., a (3,+1) ring critical point) in the center. The molecule contains four conventional, although slightly polarized B-Be bonds. A combination of some of the B<sub>4</sub> and B<sub>2</sub>Be<sub>2</sub> features is found in B<sub>2</sub>Li<sub>2</sub>. This cluster has two highly curved B-B bond paths, each containing two bond critical points. The center between the borons also contains a bond critical point which connects the "pseudo atoms" on the two B-B bond paths, to which also the two lithiums are bonded. This structure has no bonding at the circumference and is highly ionic.

# Laplacian plots of Diborides

## Molecular Graphs of Diborides at the Molecular Plane

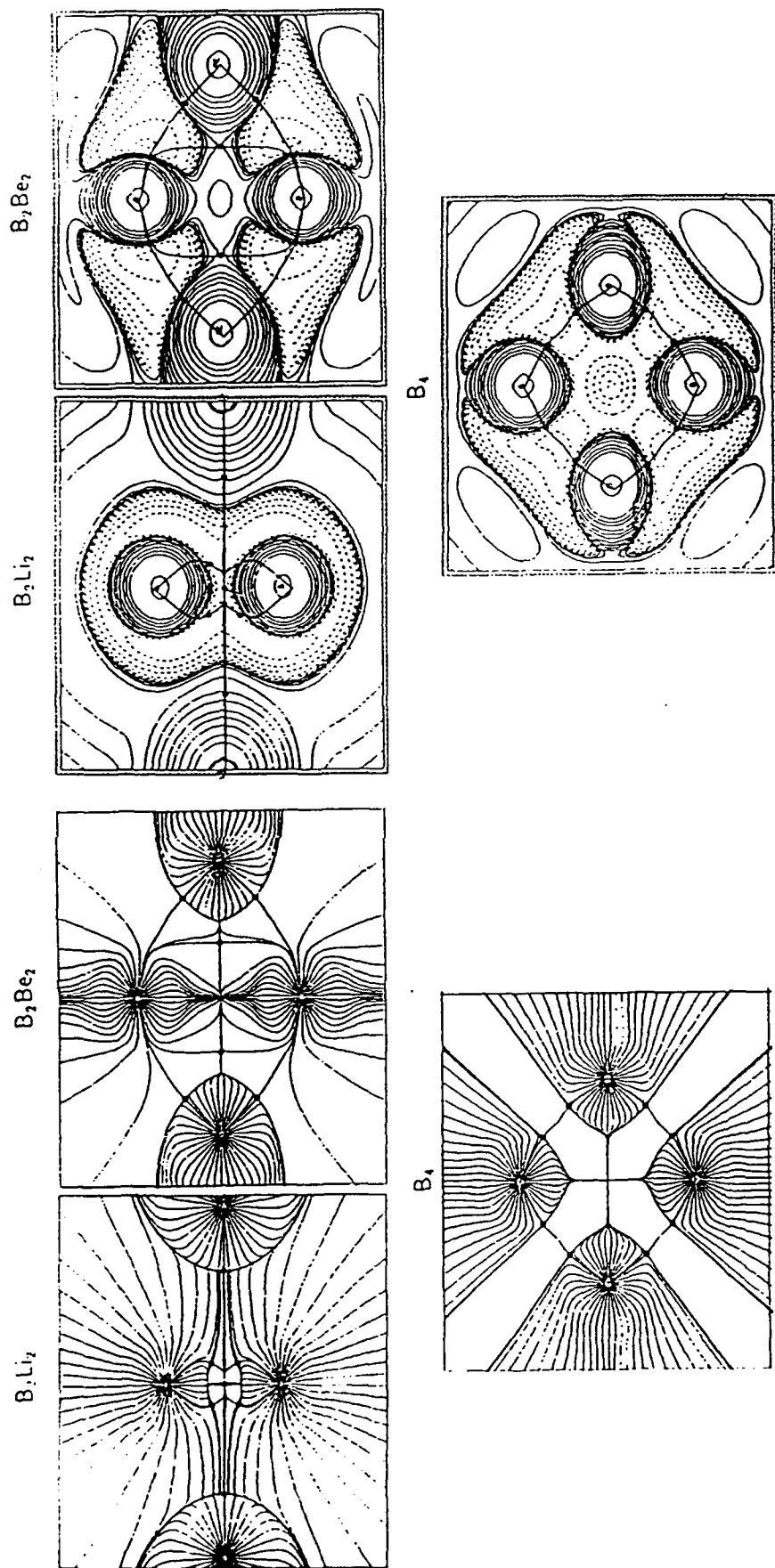


Figure 3. Gradient vector field and the Laplacian concentration of the HF/6-31G\* charge density of  $B_2Li_2$ ,  $B_2Be_2$ , and  $B_4$ .

This analysis and the comparison with diborides makes clear that these tetraatomic diboride clusters have special bonding features, which were as of yet undiscovered. In our opinion we have just scratched the surface of the bonding features possible for boron based clusters. A more detailed study of  $B_2Be_2$  and  $B_2Li_2$  is given in section 2.5.2 and 2.5.3, respectively.

## TETRAHEDRAL STRUCTURES

Light elemental clusters, like the tetraatomic  $Be_4$ , may form tetrahedral structures (*vide infra*). Because several rhombic species were calculated to be transition structures we decided to evaluate tetrahedral diboride structures, which can also be considered as high density species. An incentive for this study was also provided by the fact that the above discussed rhombic structures are not necessarily the global minima. For example, linear triplets can be energetically competitive as in  $C_4$ ,  $C_4H^+$ , and  $C_4H_2^{2+}$ , (all 16 valence electrons)<sup>6</sup> and even be strongly preferred as in the 12 valence electron  $C_2Be_2$ .<sup>18</sup> The lighter 10 valence electron ionic dilithiodicarbide  $C_2Li_2$ , however, has again a rhombic structure.<sup>21</sup> Although,  $Li_4$  is also a planar rhombic (in sharp contrast to  $H_4$ ), a higher energy tetrahedral form is also feasible.

We calculated 24 tetrahedral-like diborides at the HF/6-31G\* level of theory. Their geometries and energies are listed in Table 4. Of the 24 structures 9 are minima ( $B_2Li_2$ ,  $B_2Be_2$ , and  $B_2Be_2H^-$ ) and 16 are transition structures. This data shows that densely packed tetrahedral structures are preferred for certain light elemental combinations.

## ESTIMATED SPECIFIC IMPULSES

Having established that rhombic carbon structures are of high energy, and having determined that indeed a large variety of tetraatomic rhombic and some tetrahedral clusters are minima (but not necessarily global minima) on the potential energy surface, a crude estimate of their specific impulses can be obtained with the following formula:

$$I_{sp} = 265 \times \sqrt{[(\text{heat of formation})/(\text{mol. weight})]}$$

The heat of formation is estimated from our ab initio calculated binding energy and the heats of formation of gaseous atoms from elements in their standard states. In Table 5 ab initio energies (MP4 and HF/6-31G\*) of rhombic structures are used except for  $B_2Be_2$  for which the more stable tetrahedral-like isomer was used (*vide infra*).

TABLE 4. Tetrahedral Diborides RHF/6-31G\* Energies, NIMAG and Geometrical Data.

Structure X-B <sub>2</sub> -Y	Energy	Nimag	Bond Distances			
			B—B	B—X	B—Y	X—Y
Li-(B <sub>2</sub> )-Li	-64.06043	0	1.548	2.252	2.252	3.504
Be-(B <sub>2</sub> )-Be	-78.37354	0	1.548	1.772	1.772	2.156
Be-(B <sub>2</sub> )-BeH	-79.01726	0	1.529	1.802	1.926	2.447
Be-(B <sub>2</sub> )-BH	-88.99520	1	1.520	1.764	1.653	2.131
Be-(B <sub>2</sub> )-CH	-101.87523	1	1.447	1.962	1.717	1.571
Be-(B <sub>2</sub> )-C:	-101.50896	1	1.484	2.102	1.511	1.557
Be-(B <sub>2</sub> )-AlH	-306.26094	1	1.544	1.766	2.049	2.554
Be-(B <sub>2</sub> )-Si:	-352.64423	1	1.524	1.763	1.993	2.569
BeH-(B <sub>2</sub> )-BH	-89.64323	2	1.531	1.903	1.625	2.226
BeH-(B <sub>2</sub> )-CH	-102.74791	2	1.525	2.173	1.480	1.852
BeH-(B <sub>2</sub> )-AlH	-306.90465	1	1.535	1.927	1.994	2.752
BH-(B <sub>2</sub> )-BH	-99.59929	2	1.567	1.656	1.656	1.908
BH-(B <sub>2</sub> )-CH	-112.51562	1	1.427	1.884	1.675	1.450
BH-(B <sub>2</sub> )-AlH	-316.87552	1	1.528	1.660	2.038	2.404
BH-(B <sub>2</sub> )-Si:	-363.24008	2	1.445	1.844	2.259	1.945
CH-(B <sub>2</sub> )-CH	-125.16082	1	1.447	1.716	1.716	1.340
CH-(B <sub>2</sub> )-C:	-125.00759	1	1.430	1.682	1.687	1.342
CH-(B <sub>2</sub> )-AlH	-329.75801	1	1.500	1.502	2.246	2.129
CH-(B <sub>2</sub> )-Si:	-376.15976	1	1.433	1.654	2.332	1.826
:C-(B <sub>2</sub> )-C:	-124.61891	2	1.407	1.750	1.750	1.383
:C-(B <sub>2</sub> )-AlH	-329.40172	1	1.488	1.516	2.405	1.814
AlH-(B <sub>2</sub> )-AlH	-534.14341	1	1.538	2.043	2.043	2.912
AlH-(B <sub>2</sub> )-Si:	-580.52553	1	1.526	2.040	1.997	2.823
:Si-(B <sub>2</sub> )-Si:	-626.90122	1	1.458	2.135	2.135	2.364

TABLE 5. Estimated  $I_{sp}$  values.<sup>a</sup>

System	Binding Energy		Specific Impulse	
	(kcal/mol)		(sec)	
	MP4	HF	MP4	HF
B <sub>2</sub> Li <sub>2</sub>	178.5	87.8	591	727
B <sub>2</sub> Be <sub>2</sub>	195.4	122.7	646	738
C <sub>4</sub>	576.4	496.8	399	524
C <sub>2</sub> Si <sub>2</sub>	379.0	415.5	396	354

These data confirm our supposition that rhombic structures indeed have large estimated  $I_{sp}$  values and that, as expected, they are largest for those systems that are composed of elements with the highest combustion energies. The data for B<sub>2</sub>Li<sub>2</sub> and B<sub>2</sub>Be<sub>2</sub> also demonstrate the significant influence of electron correlation in determining calculated binding energies. Therefore, the given  $I_{sp}$  values are only rough estimates, because of the direct relationship between the estimated magnitude of the specific impulse and the accuracy of the calculated binding energy.

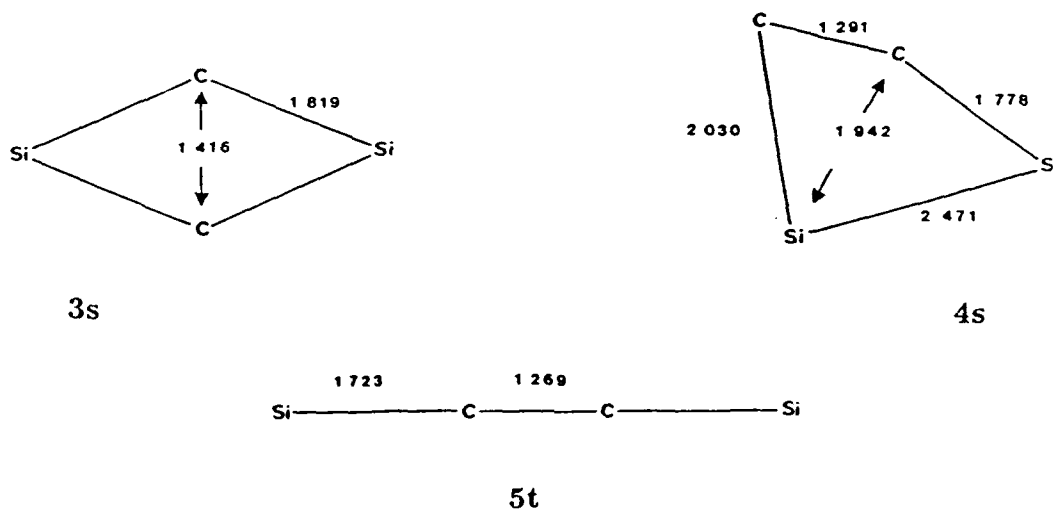
## CLUSTER MOLECULES – Potential Energy Surfaces

In this section we elaborate in more detail the potential energy surfaces for a selected group of tetraatomics. Although we have demonstrated that most rhombic structure are viable species (minima), it is also apparent that they need not be the global minima. To further evaluate the potential of rhombic (or tetrahedral) species for consideration as high energy density systems, it is relevant to investigate more fully the structures of certain elemental combinations. We report here our analysis of C<sub>2</sub>Si<sub>2</sub>, B<sub>2</sub>Be<sub>2</sub>, B<sub>2</sub>Li<sub>2</sub>, and Li<sub>3</sub>H, which cover a group of widely different species ranging from light to heavy elemental combinations.

**Disilicondicarbide, Si<sub>2</sub>C<sub>2</sub>.** Our first objective was to investigate a binary cluster for its structural, energetic, and electronic properties. As already noted, the 16 valence electron C<sub>4</sub> shows a slight preference for the rhombic over linear structure, which reverses on mono- and diprotonation to C<sub>4</sub>H<sup>+</sup> and to C<sub>4</sub>H<sub>2</sub><sup>2+</sup>.<sup>6</sup> In contrast, the related 16 electron Si<sub>4</sub> strongly favors a rhombic form,<sup>22</sup> with its 20 electron tetraanion Si<sub>4</sub><sup>4-</sup> fragment being tetrahedral.<sup>23</sup> It is well recognized that the bonding properties of silylenes differ significantly from those of the corresponding carbon compounds.<sup>3</sup> It is then relevant to investigate the properties of a mixed cluster that contains both C and Si. We give here a very brief summary of our investigation of the potential energy surface for the C<sub>2</sub>Si<sub>2</sub>

system. A full description of this work has appeared in the literature<sup>24</sup> and is attached in appendix B.

The structures and energies of the binary disilicon dicarbide  $C_2Si_2$  in the lowest singlet (s) and triplet (t) states (14 isomers) were investigated by ab initio MO theory. Full fourth-order Møller-Plesset (MP4) perturbation theory was employed on seven HF/6-31G\* optimized geometries. Rhombic dicarbide **3s** is the global minimum and 8.5 kcal/mol more stable than the rhomboidal structure **4s**, which contains an inverted tricoordinate carbon as well as an inverted tricoordinate silicon. Both cyclic structures are energetically favored over a linear triplet isomer **5t**. Whereas the relative energies are very sensitive to electron correlation effects, addition of diffuse functions (MP2 and HF/6-31+G\*) has little influence.

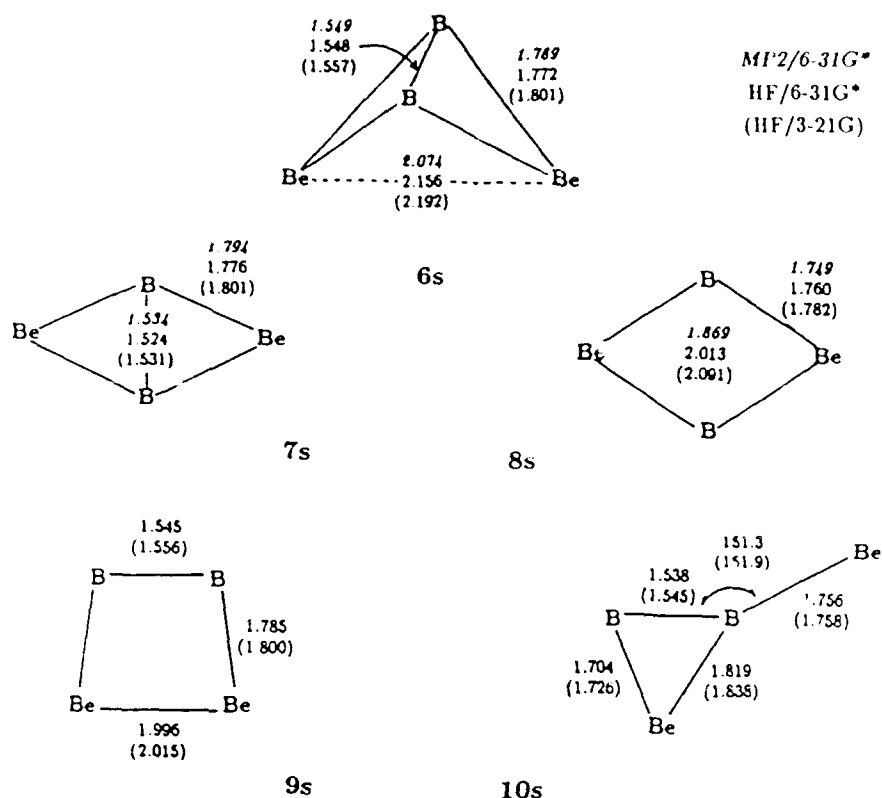


This study shows that disilicon dicarbide has similarities with the related  $C_4$  and  $Si_4$  but also that it is inherently more complex; an important aspect of this will be emphasized in section 2.6. We note that there is an isoelectronic relationship between **3s** and the rhombic  $Al_2Si_2^{2-}$  fragment in the  $CaAl_2Si_2$  material,<sup>25</sup> which is representative for a large class of solid Zintl complexes.<sup>26</sup> The rhomboidal structure **4s**, with its mixed C/Si bonding, is also unique to binary clusters and similarly may well be an important structural type.



**Diberylliumdiboride,  $B_2Be_2$ .** This 10 valence electron species is composed of the two elements with the highest combustion energies. Because of its anticipated importance as a high energy material,  $B_2Be_2$  was subjected to a full (singlet *s* and triplet *t*) potential energy surface study to characterize its global minimum, to determine its stability, and to investigate its binding energies and properties. Because of its smaller difference in elemental electron negativities than that in the isoelectronic dilithium dicarbide ( $C_2Li_2$  has a preferred ( $6^\circ$ ) puckered rhombic structure)<sup>21</sup> and the 12 val. el. diberyllium dicarbide  $C_2Be_2$ ,<sup>18</sup> the properties of  $B_2Be_2$  were expected to deviate from  $C_2Li_2$ ,  $C_2Be_2$ , and other tetraatomics. Beryllium borides are known since the turn of the century with crystal structures (powder patterns) reported for  $BBe_6$ ,  $BBe_3$ ,  $BBe_2$ ,  $B_2Be$ ,  $B_4Be$ ,  $B_6Be$ ,  $B_8Be$ ,  $B_{10}Be$ , and  $B_{12}Be$  with the noticable exception of  $B_2Be_2$ .<sup>27</sup> Here we give here a very brief summary of our study of the  $B_2Be_2$  system. A full analysis is given in Appendix C and is to appear in the literature.<sup>28</sup>

The ab initio molecular orbital study of the 10 val. el. diberyllium diboride ( $B_2Be_2$ ) potential energy hypersurface yields a singlet tetrahedrallike form **6s** as the global minimum at the HF and MP2/6-31G\* levels of theory. At MP4/6-31G\* the energy difference of **6s** with any other isomer is at least 30 kcal/mol; (high spin-contamination in triplet structures was annihilated). The topological electron density analysis, based on the theory of atoms in molecules, shows **6s** to have its Be atoms polar  $\pi$ -complexed to the B-B bond with an angle of  $80.1^\circ$  between the  $\pi$  planes; despite the short 2.156 Å Be-Be distance, there is no Be-Be bond. The inversion barrier ( $6s \rightleftharpoons 7s \rightleftharpoons 6s$ ) amounts to 11.7 kcal/mol at MP4/6-31G\* + ZPE and 14.6 kcal/mol at MP2/6-311G(df) + ZPE. The  $D_{2h}$  structures **7s** and **8s** are related by means of "bond-stretch" isomerism. The electron density analysis shows that the electron density is concentrated in the center of structures **7s** whereas **8s** shows a depletion of electron density in the center as compared to the periphery of this rhombic structure. The trapezoidal **9s** and the Be-substituted  $B_2Be$  ring **10s** are discussed for their structural and electronic properties. All  $B_2Be_2$  structures show short B-B bonds (i.e., 1.549 Å for **6s**, MP2/6-31G\*) with the exception of **8s** (1.869 Å, MP2/6-31G\*). The effects of electron correlation on relative energies and binding energies is significant. The binding energy of the four elements in **6s** is 204 kcal/mol and that of one beryllium in **6s** is 76 kcal/mol (all MP4/6-31G\*). A calculated specific impuls for **6s** is given in section 2.4.



From this study we infer that the nature of bonding (covalent and ionic complexation) is an important aspect for the formation of large clusters that may form molecular solids. This supports the finding of Dr. Brener's at the Louisiana State University that larger clusters (molecular solids) of the tetrahedral  $B_2Be_2$  unit cell are favorable.<sup>25</sup>

**Dilithiodiboride,  $B_2Li_2$ .** Both finely dispersed Li and boron compounds are known to boost the performance of rocket fuels. Therefore, our next step was to investigate the properties of the even lighter tetraatomic system, the 8 val. el dilithio diboride  $B_2Li_2$ .

An ab initio molecular orbital study was performed on the  $B_2Li_2$  singlet and triplet potential energy hypersurface. The singlet rhombic form 11s is the global minimum at the HF and MP4/6-31+G\* levels of theory of the 10 isomers investigated. Figure 4 displays the HF/6-31G\* optimized structures. At the correlated level this isomer is favored by 8.3 kcal/mol over the tetrahedral isomer and by at least 20 kcal/mol more than any other isomer. However, the data listed in Table 6 show a rather strong oscillation between the MP2, MP3, and MP4 relative energies for 11s and 12s, indicating that probably a multireference wave function is required for determination of accurate energies. The effects of electron correlation on all relative energies is very significant as graphically shown in Figure 5. A calculated specific impuls for 11s is given in section 2.4.

TABLE 6. Total (au) and Relative (kcal/mole) Energies of  $\text{Li}_2\text{B}_2$  Isomers

Structure	HF/6-31G*	Rel. En.	NIMAG	$\langle s^2 \rangle$	MP4/6-31G*	Rel. En.
11s	-64.04676	0.0	(0)		-64.30754	0.0
11t	-64.05044	-2.3	(0)	2.03	-64.25693	31.8
12s	-64.06043	-8.6	(0)		-64.29335	8.9
12t	-64.08114	-21.6	(1)	2.25	-64.26819	24.7
13s	-64.05724	-6.6	(0)		-64.24349	40.3
13t	-64.03463	7.6	(2)	2.03	-64.23644	44.6
14s	-64.01299	21.2	(2)		-64.24051	42.1
15t	-64.07447	-17.4	(0)	2.21	-64.25147	35.2
16t	-64.08134	-21.7	(0)	2.05	-64.26682	25.6
17t	-64.06390	-10.8	(1)	2.05	-64.25268	34.4

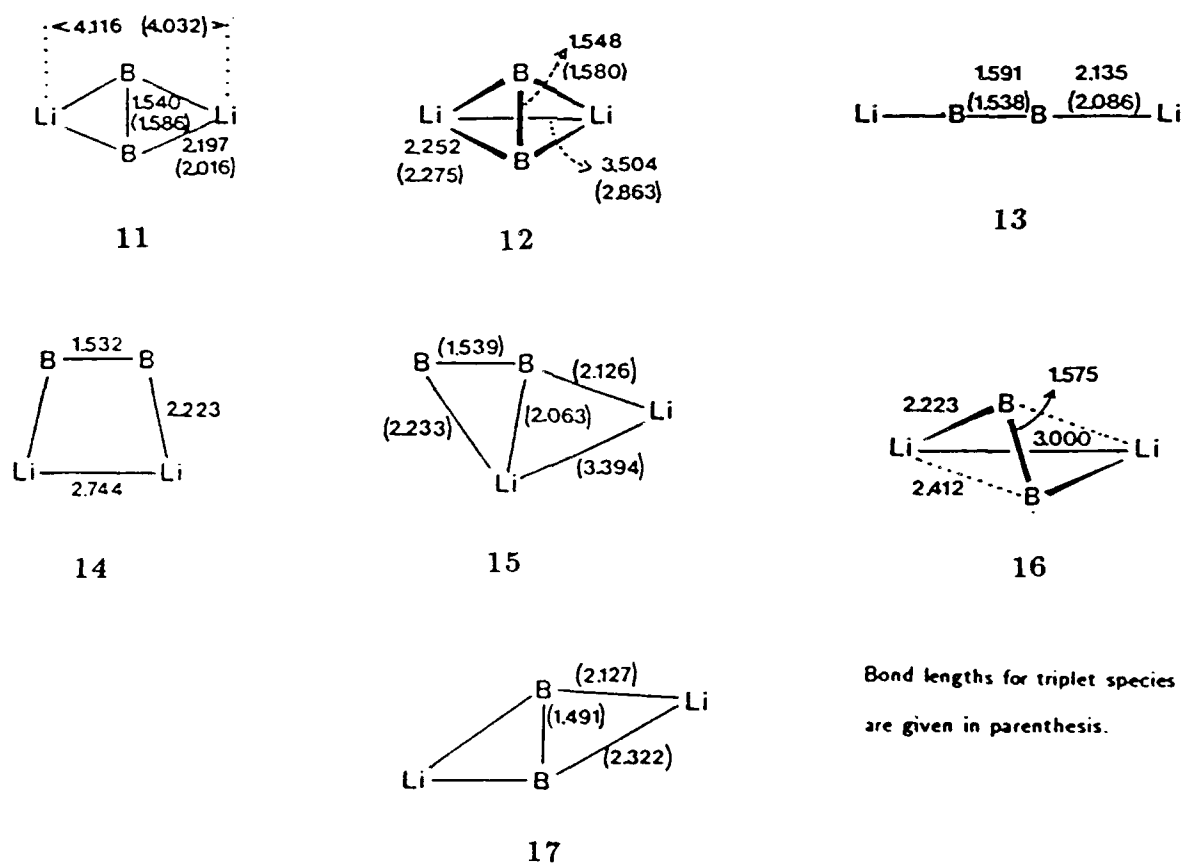


Figure 4. HF/6-31G\* geometries of  $\text{B}_2\text{Li}_2$  isomers.

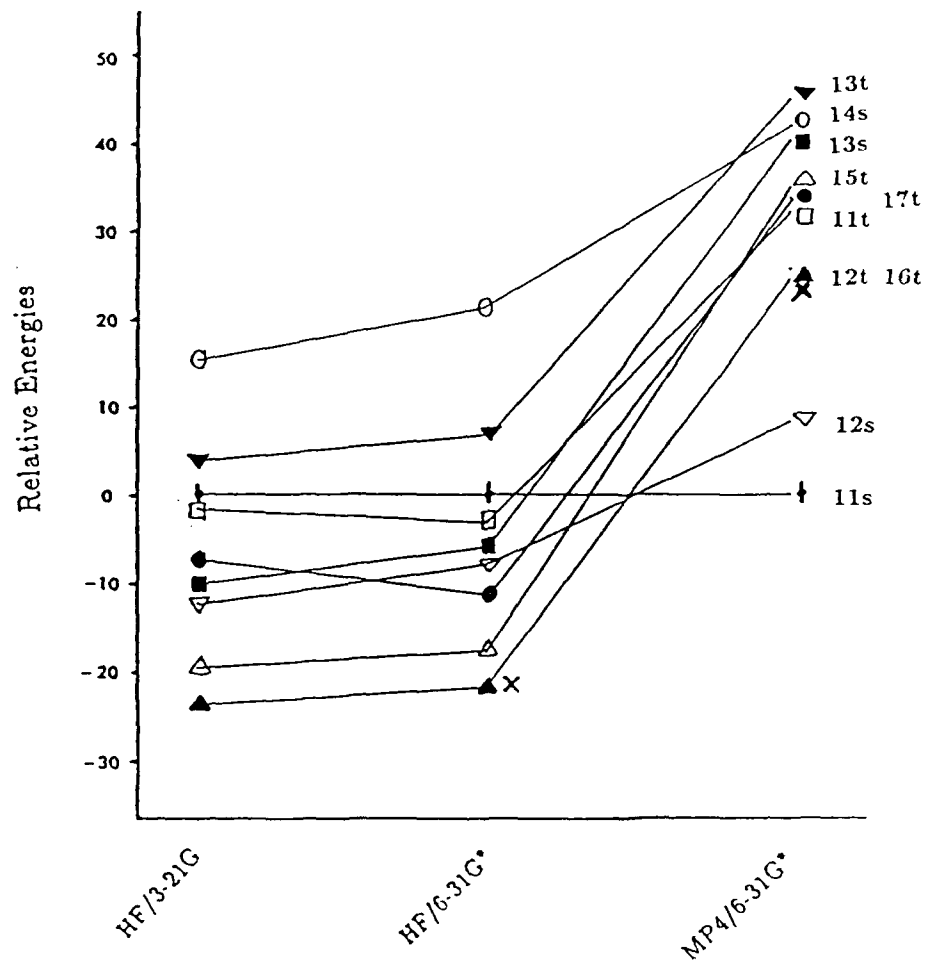


Figure 5. Plot of relative  $B_2Li_2$  energies basis set.

The topological electron density analysis for the rhombic  $B_2Li_2$  structure shows that the Li atoms complex ionically to the  $B_2$ -unit. This is evident from the gradient vector field and the Laplacian of  $\rho$ , which are displayed in Figure 6. The molecular graph for **11s**, also displayed in Figure 6, shows a complex topology. This probably results from the use of a limited basis set (MP2/6-31+G\*) to describe the electron density properties of the electron-rich  $B_2^{2-}$  group. The bond properties for **11s** and **12s** are listed in Table 7.

**The  $Li_3H$  Ion-Pair** This study was performed in collaboration with J.A. Montgomery and H.H. Michels of United Technology Research Center. Our interest in this 4 val. el. system relates to the chemistry of small clusters and ion-pair states. A full analysis of our study, which has appeared in the literature,<sup>30</sup> is given in Appendix D. A brief abstract of the work follows.

Ab initio calculations on  $Li_3H$  ion-pair states and a topological analysis of the charge density of the resulting optimized structures are reported. The global  $Li_3H$  minimum is a planar  $C_{2v}$  structure with  $H-Li_3^+$  ion-pair character. The pyramidal  $C_{3v}$  structure, which is 21.5 kcal/mol higher in energy (MP2/6-311++G\*\*), is found to have ionic H-Li bonds, but no Li-Li bonds. Although vibrational analysis indicates this structure to be a true minimum on the potential energy surface, inclusion of the vibrational zero-point energy makes the thermodynamic stability of this structure questionable.

## BOND-STRETCH ISOMERISM

In the course of this work we determined that many tetraatomic systems may have the properties of bond-stretch isomerism. We resorted to the  $C_2Si_2$  and  $B_2Be_2$  systems to analyze this phenomenon in more detail and to establish its value in small cluster molecules. The properties of the  $B_2Be_2$  system have been fully analyzed in the already discussed  $B_2Be_2$  potential energy surface study that is given in Appendix C.<sup>28</sup> The study of the bond stretch isomerism in  $C_2Si_2$  is discussed separately in full detail in Appendix E. A brief abstract of this published research<sup>31</sup> follows.

The differences in bonding and electronic properties between the MP2/6-31G\* optimized disilicon dicarbide structures **3** and **18** can be related to bond stretch isomerism, which occurs through a level-crossing mechanism. Their energy differences are calculated to be 78.4 at the MP4 and 91.4 kcal/mol at GVB/6-31G\*. Because of the symmetry forbidden transformation no barrier for this process was calculated. Electron density analysis indicates concentration of charge in the center of rhombic structure **3** with some multiple bonding character between its transannular carbons. In contrast, the higher energy isomer

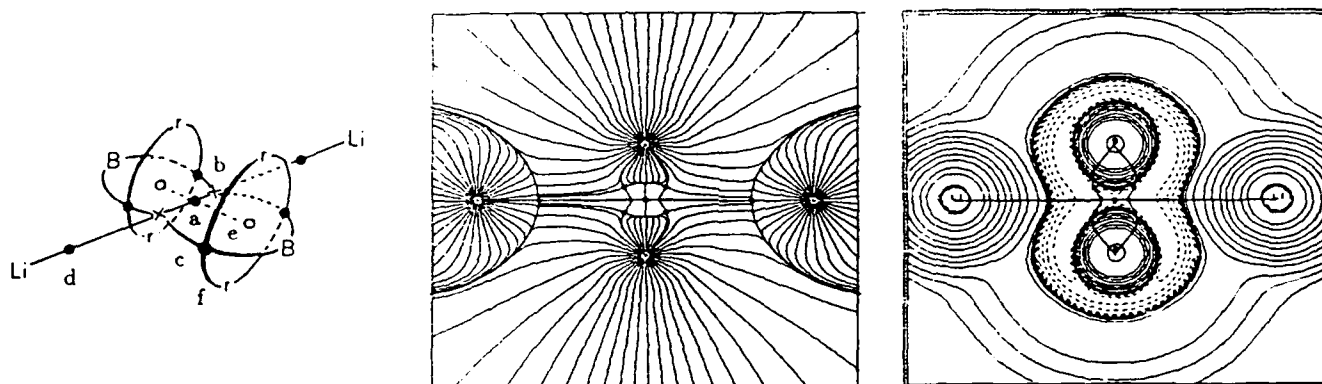
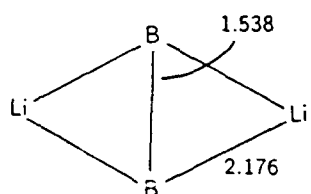
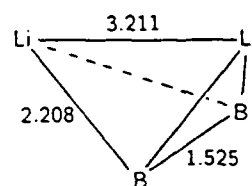


Figure 6. Molecular graph, gradient vector field, and the Laplacian concentration of the MP2/6-31+G\* charge density of B<sub>2</sub>Li<sup>-</sup> (11s).



11s

MP2/6-31+G\* D<sub>2h</sub>

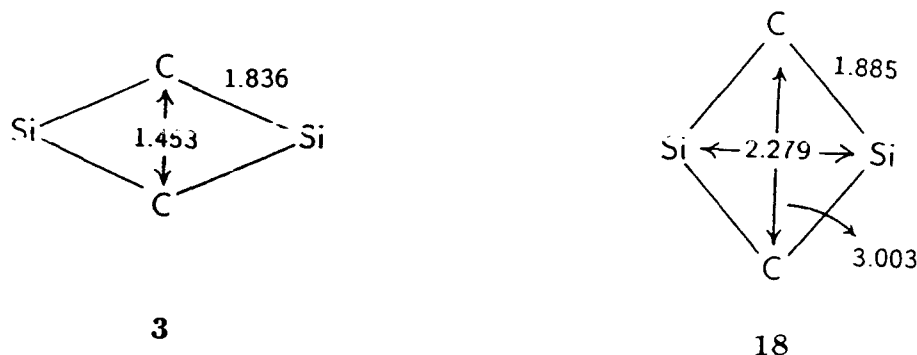


12s

MP2/6-31+G\*  $\angle \alpha = 101.6$

TABLE 7. MP2/6-31+G\* Bond Properties for 11s and 12s

Struct./Crit.Pt.	Type	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\epsilon$	<i>dir</i>	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$H(\mathbf{r})$	
11s	a	[3,-1]	-1.21	-0.40	0.32	2.09	$\perp$	0.73	-1.28	-0.60
	b	[3,-3]	-0.67	-0.64	-0.58	0.04	$\parallel$	0.73	-1.89	-0.57
	c	[3,-1]	-1.90	-0.65	0.67	1.94	$\perp$	0.73	-1.88	-0.61
	d	[3,-1]	-0.80	-0.43	4.66	0.87	$\parallel$	0.21	3.43	0.02
	e	[3,+3]	0.28	1.10	5.33	-	-	0.71	6.70	-0.56
	f	[3,+1]	-1.55	0.76	3.20	-	-	0.71	3.41	-0.59
12s	a	[3,-3]	-5.87	-3.10	-0.33	0.89	$\perp$	1.09	-9.29	-0.95
	b	[3,-1]	-6.35	-3.05	2.92	1.08	$\perp$	1.08	-6.48	-1.13
	c	[3,-1]	-0.65	-0.23	3.63	1.80	$\perp$	0.18	2.75	0.01



18 has a depletion of charge in the center relative to the circumference of the rhombic structure.

## HYDROGENATED TETRAATOMICS

Another question we addressed concerns the effect of hydrogen substitution on small inorganic clusters. In contrast to the extensive literature on carbon systems, very little is known about the related inorganic systems. In light of the special bonding characteristics associated with  $B_2Be_2$  (section 2.5.2) we decided to investigate the effect of its hydrogenation. Since boranes are energetic materials and because little is known about alanes we also explored  $Al_2H_6$ . The latter research is a first step to a closer investigation of rhombic and tetrahedral diborides with bridging aluminum ligands.

**Hydrogenated Diberyllium Diboride,  $B_2Be_2H_2$ .** An ab initio molecular orbital study was performed on the  $B_2Be_2H_2$  singlet potential energy hypersurface. Structure 19 is the global minimum of the eight isomers analyzed. These eight HF/6-31G\* optimized  $B_2Be_2H_2$  structures are shown under Table 8 that lists their total and relative energies at the HF and MP4/6-31G\* levels. At the correlated level 19 is energetically favored by at least 14 kcal/mol over any other isomer. It is also evident that the effect of electron correlation is much less pronounced than was the case in the hydrogen-void  $B_2Be_2$  system. However, the geometries and the data listed in Table 8 also indicate special properties related to the hydrogenation of tetrahedral/rhombic  $B_2Be_2$ . For example, the energy difference between hydrogenation on the borons versus hydrogenation on beryllium (which formally become tricoordinate) amounts to only 15 kcal/mol.

It appears that hydrogenation of  $B_2Be_2$  is preferred on both borons followed by hydrogenation on the two berylliums. The global minimum 19 can be regarded as a diborane(2)

complexed with two beryllium atoms. Consequently, structure **19** would also be a very energetic system. We anticipate that similar to the tetrahedral-like  $B_2Be_2$  isomer also **19** will not contain Be-Be bonding (despite the 1.886 Å separation) but instead will have its berylliums complexed to the center of the 1.764 Å B-B bond. The 'second best' structure is ca. 15 kcal/mol less stable than **19** and contains a 1.5 Å short B-B bond with bridging Be-H groups in either a planar (**22**) or 'butterfly' (**21**) orientation; the nature of the stationary point must be determined at correlated levels. Clearly, the bonding characteristics of this system warrant further investigation.

**Dialane(6),  $Al_2H_6$ , and Digallane(4),  $Ga_2H_4$ .** In contrast to the vast amount of literature on small boranes, carbon, and silicon molecules, only very little is known on small aluminum based molecules. Since aluminum, for a second row element, has a rather high combustion energy and because of its likely suitability (as boron) to form high density materials, we decided to investigate the experimentally still elusive dialane(6). An additional incentive for this study was the recent experimental observation of digallane(6).<sup>32</sup> Therefore, a theoretical study on  $Al_2H_6$  and  $Ga_2H_6$  would enable us to calibrate the ab initio data against experimental  $Ga_2H_6$  values as well as to determine the binding energy and bonding properties of  $Al_2H_6$ . Since we recently reported on dialane(4)  $Al_2H_4$ ,<sup>33</sup> it was also decided to study  $Ga_2H_4$  with the intention to further calibrate hydrogenated group III elements. This research is considered to be a necessary first step for closer inspection of rhombic and tetrahedral systems that contain aluminum ligands. A brief summary of our studies on  $Al_2H_6$ / $Ga_2H_6$ <sup>34</sup> and  $Ga_2H_4$ <sup>35</sup> follows. The full analysis of these systems is given in Appendix F and G, respectively, which are to appear in the literature.

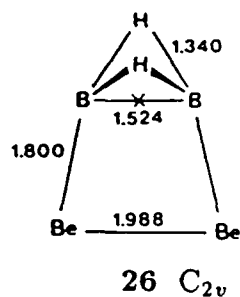
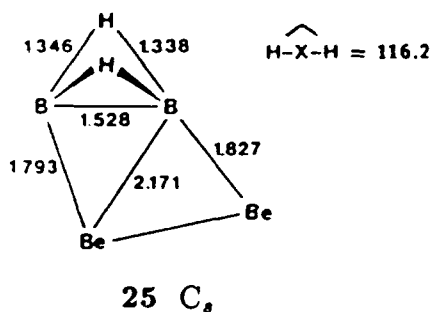
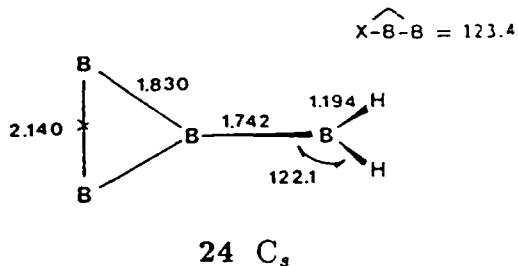
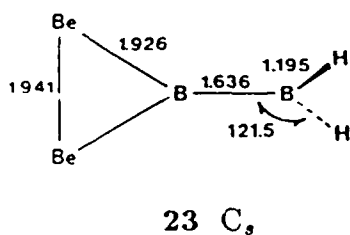
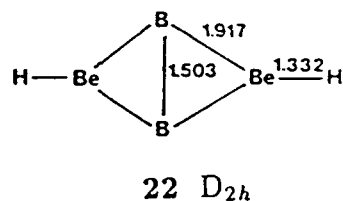
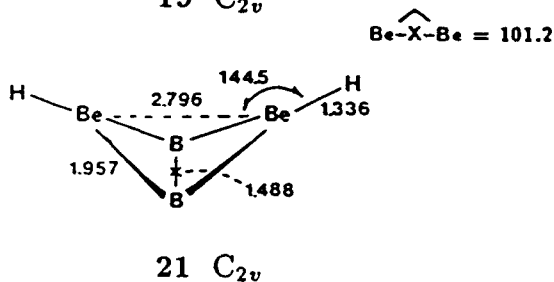
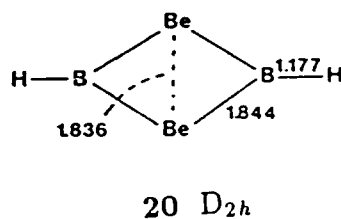
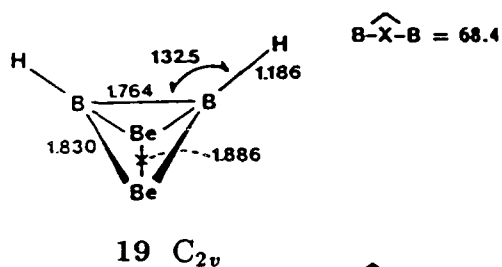
The structure, harmonic frequencies, and binding energies of dialane(6) and digallane(6) are calculated with ab initio MO theory. Excellent agreement is found with IR spectroscopic data on  $Ga_2H_6$ . The binding energy for  $Al_2H_6$  is 31.5 kcal/mol at MP4/6-31G\*\* and for  $Ga_2H_6$  a value of 23.4 kcal/mol is obtained with a Huzinaga valence triple  $\zeta$  basis set after correction for ZPE and electron correlation effects at MP4.

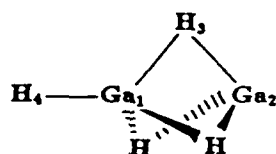
The potential energy surface of digallane(4)  $Ga_2H_4$  has been studied by ab initio molecular orbital theory at the MP2 level using a Huzinaga valence triply  $\zeta$  basis set supplemented with d-polarization functions. Six of the eight HF/3-21G\* optimized structures were characterized as minima. Their bonding properties were studied by a topological electron density analysis. Of the ionic, covalent, and  $\mu$ -hydrido bridged species the tri- and bidentate  $Ga^+[GaH_4]^-$  forms **27** and **28**, respectively, are the most stable isomers. However, the energy differences with the other isomers are less than 15 kcal/mol. The



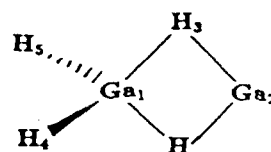
TABLE 8. Total (au) and Relative (kcal/mole) Energies of B<sub>2</sub>Be<sub>2</sub>H<sub>2</sub> Isomers.

Structure	Tot. En.	Rel. En.	NIMAG	Tot. En.	Rel. En.
19 C <sub>2v</sub>	-79.62424	0.0	(0)	-79.93443	0.0
20 D <sub>2h</sub>	-79.56060	39.9	(0)	-79.89878	22.4
21 C <sub>2v</sub>	-79.59930	15.7	(0)	-79.91033	15.1
22 D <sub>2h</sub>	-79.58958	21.8	(1)	-79.91144	14.4
23 C <sub>s</sub>	-79.58598	24.0	(0)	-79.85155	52.0
24 C <sub>s</sub>	-79.55500	43.5	(1)	-79.84456	56.4
25 C <sub>s</sub>	-79.53958	53.0	(0)	-79.83565	62.0
26 C <sub>2v</sub>	-79.53812	54.0	(1)	-79.83335	63.4

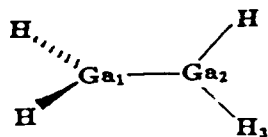




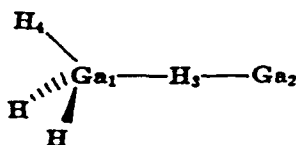
27  $C_{3v}$



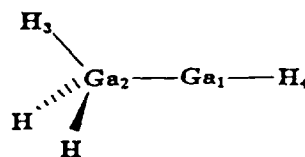
28  $C_{2v}$



29  $D_{2d}$



30  $C_{3v}$



31  $C_{3v}$

The potential energy surface of digallane(4)  $Ga_2H_4$  has been studied by ab initio molecular orbital theory at the MP2 level using a Huzinaga valence triply  $\zeta$  basis set supplemented with d-polarization functions. Six of the eight HF/3-21G\* optimized structures were characterized as minima. Their bonding properties were studied by a topological electron density analysis. Of the ionic, covalent, and  $\mu$ -hydrido bridged species the tri- and bidentate  $Ga^+[GaH_4]^-$  forms 27 and 28, respectively, are the most stable isomers. However, the energy differences with the other isomers are less than 15 kcal/mol. The covalent  $D_{2d}$  isomer 29 is 3.5 kcal/mol less stable than 27. The head and tail complexes of  $:GaH$  with  $GaH_3$  (30 and 31), which are of similar energy, are ca. 13 kcal/mol higher in energy than 29. The potential energy surface of  $Ga_2H_4$  is similar to that of  $Al_2H_4$  but differences are noted.

## CONCLUSIONS AND RECOMMENDATIONS

The main conclusions from our general survey on small cluster molecules (ca 60) and from our studies on seven selected systems are as follows:

The ab initio molecular orbital study on tetraatomic systems has shown that 24 of the 25 investigated rhombic dicarbides and 21 of 28 studied rhombic diborides are local or global minima on the potential energy structures. This confirms the general viability of rhombic clusters composed of the elements H, Li, Be, B, C, Al, and Si. We found that only the rhombic, tetrahedral, and (triplet) linear structures compete for the global minima. Only 3 tetrahedral (light) diboride clusters out of 24 combinations are equilibrium structures. We have also demonstrated the high energy content in these rhombic and tetrahedral clusters, which are composed of high combustion light elements. The most energetic systems investigated (MP4/6-31G\*\*//MP2/6-31G\*) are  $B_2Li_2$  and  $B_2Be_2$ . They have the highest estimated  $I_{sp}$  values (591 seconds and 646 seconds, resp.).

The general survey study also establishes that the bonding character between the bridgehead atoms (B or C) in rhombic and tetrahedral structures varies widely (i.e., from double bonding to no bonding) and depends on the nature (electronegativity) of the bridging ligands. For example, rhombic  $C_4$  has no transannular bonding, but  $C_2Be_2$  has strong C-C bonding as does  $C_2Si_2$ . Similarly  $B_4H_2$  has no transannular bonding, but in  $B_2Li_2$  there is a multiple B-B bond.

The potential energy surface studies on  $B_2Li_2$ ,  $B_2Be_2$ ,  $Li_3H$ , and  $C_2Si_2$  demonstrate an extreme sensitivity of these tetraatomics to the effects of electron correlation.

Bond-stretch isomerism is a likely mechanism for energy storage and is common to the frame of rhombic tetraatomics as demonstrated in  $B_2Be_2$  and  $C_2Si_2$ . Such isomers have large energy differences and are separated by level crossing mechanisms, implying that the high energy isomers lie in deep potential wells.

To study the structural, energetic, and electronic properties of small clusters, composed of light elements, the total electron density of such systems must be analyzed in combination with standard ab initio molecular orbital analysis.

The main recommendations from this research toward high energy density materials are:

- (a). Higher levels of theory are required as well as a mapping of all dissociation modes for the light elemental clusters (H, Li, B, and Be) to obtain kinetic and thermodynamic data of enough accuracy to predict reliable  $I_{sp}$  values.
- (b). More work is required to predict the stabilities and properties of small clusters in conventional fuel systems.
- (c). An in-depth study of the scope of bond-stretch isomerism is needed both to evaluate its potential as an energy promoting mechanism and to find practical systems that serve as energy storage devices.

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## APPENDIX A

### PUBLICATIONS

The significant research results obtained under this contract have been prepared for publication in technical journals. These papers are listed below. All of these papers can be found in the open literature.

#### Technical Reports in Journals:

1. "Structures and Energies of Disiliciumdicarbide,  $C_2Si_2$ ". K. Lammertsma and O.F. Guner. J. Am. Chem. Soc. 110, 5239-5245(1988).
2. "Bond Stretch Isomerism in Rhombic  $C_2Si_2$ ". K. Lammertsma and O.F. Guner. J. Phys. Chem. 8, 7289-7292(1989).
3. "The Structure and Bonding of  $Li_3H$  Ion-Pair States". J.A. Montgomery, Jr., H.H. Michels, O.F. Guner and K. Lammertsma. Chemical Physics Letters 161, 291-295 (1989).
4. "Structural and Electronic Properties of the Tetra-atomic  $B_2Be_2$  Cluster". K. Lammertsma and O.F. Guner. J. Am. Chem. Soc. 112, 508-516(1990).
5. Ab Initio Study on Dialane(6) and Digallane(6)". K. Lammertsma and J. Leszczynski. J. Phys. Chem. 94, 2806-2809(1990).
6. "Rhombic  $C_4$ : Does it Contain the Shortest Non-bonding C-C Distance". K. Lammertsma, O.F. Guner, and P.V. Sudhakar. To be submitted to J. Am. Chem. Soc., 1990.